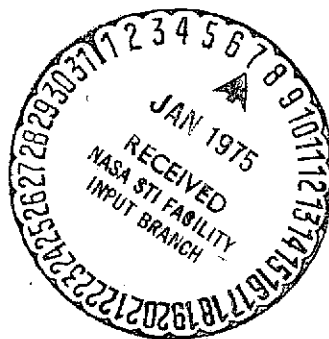


THE EFFECTS OF CARBIDE STABILIZING ELEMENTS Ti, Nb and V
ON THE HIGH TEMPERATURE STRENGTH AND MICROSTRUCTURAL
CHANGE OF 18%Cr-10%Ni AUSTENITIC STEEL

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16. Abstract The influences of titanium, niobium and vanadium on the creep rupture strength have been studied using 0.1%C-18%Cr-10%Ni stainless steels. The correlation of the strength to the microstructural change during creep has also been discussed. The highest value of 700° C-10 ⁴ hr rupture strength in a titanium and niobium series is obtained at Ti/C and Nb/C atomic ratios of 0.8 and 0.2-0.4, respectively. On the other hand, in a vanadium series, the creep rupture strength of the steel shows its maximum at V/C atomic ratio of about unity at test temperature of 700°C and 800 °C, but at 600°C, the strength increases monotonically with vanadium content up to 1.53%. The high strengths of the steels containing proper amounts of titanium, niobium, or vanadium can mainly be attributed to the fine distribution of M ₂₃ C ₆ precipitates which is caused by the acceleration of nucleation due to the foregoing precipitation of an MC type carbide within austenite grains. It is deduced that the solid solution strengthening effect of vanadium contributes also to the remarkable increase in the rupture strength of the vanadium steel at 600°C.			
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[18%Cr-10%Ni kei ōsutenaitoko no kōonni okeru kyōdo to
soshikini oyobosu tankabutsu anteika genso Ti, Nb
oyobi V no eikyō]

by

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1. Introduction

Many attempts have been made to improve the various proper-
ties of 18-8 series stainless steel, which is used as heat re-
sisting steel, by adding to it different kinds of alloying ele-
ments. These alloying elements are divided mainly into the
following 3 categories according to their behavior in steel. These
are (1) interstitial solid solution elements such as C, N and B
which are considered to dissolve interstitially in steel, (2) strong

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carbide forming elements whose solubility in austenitic (gamma) base is low and which precipitate or disperse in steel in the form of carbides, and (3) substitutional solid solution elements such as Mo, W and Cu which are mainly considered to dissolve in gamma base through substitution, although some of them do form carbides. Of these, the effects of (1), the interstitial solid solution elements, have already been examined in another report [1] which dealt with the precipitation behaviors chiefly of $M_{23}C_6$ (C, N) or $M_{23}C_6$ (C, B) and their correlation with high temperature strength. In this report, we will deal with the results of research into the effects of (2), the strong carbide forming elements.

Of the 18-8 series steels to which the strong carbide forming elements Ti and Nb have been added, 321 steel and 347 steel are respectively most widely used as heat resisting steel, and many studies [2 - 14] have been conducted regarding their high temperature strength and structural changes. These two steels were originally developed for the purpose of preventing grain boundary corrosion which accompanies the $Cr_{23}C_6$ precipitation of 18-8 stainless steel, but it is thought that they also came to be utilized as heat resisting steel because of their excellent high temperature characteristics. However, there remains the question of whether or not the quantities of added Ti and Nb in these steels, which were determined from the standpoint of grain boundary corrosion, are also optimal in terms of high temperature strength. In heat resisting steels, the precipitation of $M'_{23}C_6$ is not necessarily related with the deterioration in the quality of the materials. In fact, cases have

Table 1. Chemical composition and austenite grain size of steels used (wt %).

Steel	C	Si	Mn	Cr	Ni	N			Ti	Nb	V				Austenite grain size number*
						sol. N	insol. N	total N				Ti/C	Nb/C	V/C	
S1	0.08	0.54	1.54	18.31	9.86	—	—	0.0195	tr.	0.016	—	—	—	—	5
Ti1	0.08	0.55	1.49	18.14	9.86	0.0157	0.0061	0.0218	0.04	0.003	—	0.13	—	—	7~8
Ti2	0.08	0.52	1.43	17.73	10.09	0.0021	0.0175	0.0196	0.098	0.006	—	0.31	—	—	9
Ti3	0.08	0.52	1.47	17.81	10.09	0.0022	0.0176	0.0198	0.14	0.007	—	0.44	—	—	6~7
Ti4	0.08	0.52	1.48	17.64	10.09	0.0017	0.0157	0.0174	0.245	0.006	—	0.77	—	—	5
Ti5	0.08	0.55	1.46	17.64	10.09	0.0172	0.0075	0.0247	0.392	0.008	—	1.23	—	—	8
Ti6	0.08	0.63	1.60	18.22	9.80	0.0025	0.0228	0.0253	0.64	0.004	—	2.01	—	—	8
Ti7	0.08	0.62	1.65	18.27	9.74	0.0020	0.0113	0.0133	1.13	0.004	—	3.54	—	—	8
Nb1	0.09	0.59	1.56	17.97	10.00	0.0265	0.0003	0.0268	tr.	0.07	—	0.10	—	—	6
Nb2	0.09	0.59	1.54	19.31	9.68	0.0153	0.0025	0.0178	—	0.22	—	0.32	—	—	8
Nb3	0.10	0.60	1.57	17.73	10.00	0.0160	0.0032	0.0192	tr.	0.29	—	0.38	—	—	7~8
Nb4	0.09	0.61	1.57	17.81	10.00	0.0102	0.0057	0.0159	tr.	0.29	—	0.42	—	—	8~9
Nb5	0.09	0.60	1.50	19.06	9.66	0.0150	0.0015	0.0165	—	0.41	—	0.59	—	—	7
Nb6	0.10	0.56	1.56	17.64	9.98	0.0182	0.0042	0.0224	tr.	0.57	—	0.74	—	—	8
Nb7	0.10	0.62	1.56	19.10	9.60	0.0080	0.0092	0.0172	—	0.70	—	0.91	—	—	8~9
Nb8	0.09	0.60	1.47	19.14	9.51	0.0060	0.0125	0.0185	—	1.20	—	1.72	—	—	7~8
V0	0.12	0.65	1.40	18.36	9.57	—	—	0.021	—	—	0.01	—	—	0.02	5
V1	0.12	0.61	1.41	16.20	11.77	—	—	0.053	—	—	0.39	—	—	0.77	7~8
V2	0.11	0.62	1.45	16.20	11.66	—	—	0.053	—	—	0.75	—	—	1.61	7~8
V3	0.12	0.63	1.41	16.39	11.54	—	—	0.053	—	—	1.15	—	—	2.26	7~8
V4	0.12	0.64	1.41	16.11	11.48	—	—	0.054	—	—	1.53	—	—	3.01	8~9

* Solution treatment: 1100°C-1hr WQ

even been verified in which high temperature strength is increased significantly depending on the precipitation phase or the state of dispersion [4], so that it would seem more appropriate to add optimal quantities of Ti and Nb for obtaining a state of carbide dispersion in which creep resistance is at its highest, rather than to add adequate quantities of Ti and Nb for fixing the carbon. Nakagawa et al. [15] once made a study of the effects of Nb and Ti with respect to 18Cr-12Ni steel, but they only investigated rupture time under constant stress, and, in addition, their tests were limited to relatively short durations of under 1000 hours. It would seem, therefore, that there is a need to conduct a more detailed study which also takes the correlation with the dispersion state of the precipitated carbides into account. From this viewpoint, we attempted to examine in this report the relationship between high temperature strength and microstructure by varying the amounts of

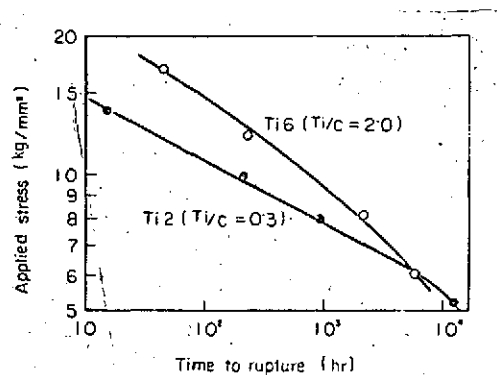


Fig. 1. Creep rupture curves of the steels Ti 2 and Ti 6 at 700°C.

added Ti and Nb over a wide range, and to determine the optimal amounts of Ti and Nb added.

V is also one of the strong carbide forming elements, but since the addition of this element causes a marked deterioration in the oxidation resistance of steels of the type in question, there have hardly been any reports on the creep rupture characteristic of austenitic steel to which V alone has been added [16]. On the precipitation of V carbides, too, there have only been a few reports [17, 18]. But with progress in research on the prevention of high temperature oxidation, it appears that it could eventually be prevented to a considerable extent through the use of coating materials, so that it can be assumed that V should be receiving attention anew as an alloying element for heat resisting austenitic steel in the future. For this reason, the effect of V on high temperature strength was also studied in this report, and the correlation with the behavior of the carbides was examined.

2. Experimental Methods and Steel Samples

For the basic composition, 18%Cr-10%Ni, which is equivalent to

regular 321 and 347 steels, was selected, and the amount of carbon was set at 0.10%, which is a little higher than normal, for the purpose of examining the effects of the carbides. The amounts of Ti added were in 7 levels from 0.04 to 1.13%, the amounts of Nb added were in 8 levels from 0.07 to 1.20%, and the amounts of V added were in 4 levels from 0.4 to 1.5%.

The samples were heated in a 50-kg high frequency furnace, and after 1 hour of solid solution heat treatment at 1100°C, they were subjected to creep rupture tests at 650°C and 700°C for the steels to which Ti and Nb have been added and at 600°C, 700°C and 800°C for the steel to which V has been added. In addition, the steels to which Ti and Nb have been added were subjected to aging treatment for 1000 hours at 700°C and observation of the structures was conducted. During this, the solid solution heat treatment was set at 1200°C and 1 hour since the objective was the observation of the precipitates. In the case of the steel to which V has been added, the aged sample was also subjected to solid solution heat treatment at 1100°C for 1 hour in order to take high temperature oxidation into account, and then aging treatment was performed at 650°C and at 700°C for up to 1000 hours. The gamma grain sizes of the steels for the 1100°C - 1 hour solid solution samples which were subjected to creep rupture tests fell within the grain size number range of 5 - 9, as indicated in Table 1.

The observation of the structures was conducted by means of an electron microscope using the extraction replica method (a Virella solution for first stage corrosion, a 10% brome alcohol solution

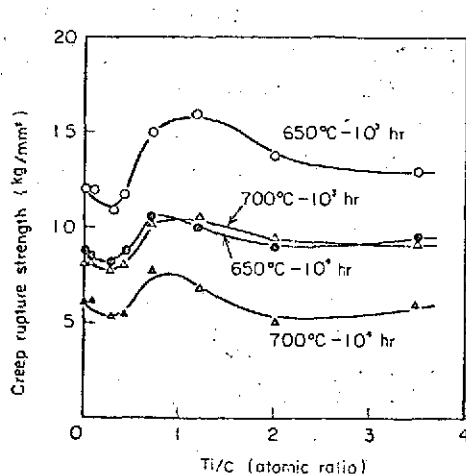


Fig. 2. Relationship between 10^3 hr rupture strength and Ti/C atomic ratio of the 16Cr-10Ni steels containing various amount of titanium.

for second stage corrosion). The samples for the scanning electron microscope and an X-ray micro-analyzer (XMA) were prepared by buffing followed by electrolytic etching using an aqueous solution of oxalic acid. The identification of the precipitates was conducted mainly by means of selected area electron beam diffraction of the extraction replica films, but transmission electron microscope observation using thin films was also conducted in some cases for verification.

The chemical compositions of the tested steels according to check analysis are shown in Table 1. The S1 and V0 steels are steels of basic compositions without the addition of Ti, Nb or V. The Ti1 to Ti7 steels with Ti added are within the Ti/C atomic ratio range of 0.13 to 3.54, and of these, Ti5 is equivalent to the regular 321 steel. There is, incidentally, considerable variance in the analytical values of the amount of insoluble nitrogen. It is believed that this insoluble nitrogen is present mainly in the form of TiN, and that consequently, the amount of effective Ti

is also affected by its quantity. But since the amount of Ti which is fixed by the 0.01% range of this variance in insoluble nitrogen is only about 0.03%, the variance in insoluble nitrogen would not seem to pose any problems during the discussion of the results of this experiment to be given later.

In the case of the Nb1 to Nb8 steels with Nb added, the Nb/C values at 0.10 to 1.72 are again well within the range in which the carbon can be fixed adequately by the Nb. The V/C values of the V1 to V4 steels with V added are from 0.77 to 3.01.

3. Experimental Results

3.1 Effects of Ti

3.1.1 Creep Rupture Strength

The creep rupture curves of the Ti2 and Ti6 steels at 700°C are indicated in Fig. 1 and show the representative behavior of steel to which Ti has been added. The Ti2 steel has a Ti/C (atomic ratio) of 0.3, but indicates an approximately linear behavior up to the vicinity of 10^4 hours. In contrast, the Ti6 steel (Ti/C = 2.0) demonstrates extremely high strength on the short time period side, but inversely, its strength shows a tendency to decline to below that of the Ti2 steel at 10^4 hours. The relationship between the Ti/C atomic ratio and creep rupture strength for these and other steels is shown in Fig. 2. The creep rupture strength values for the various steels were obtained from their creep rupture curves at 650°C and 700°C using interpolation for 10^3 hours and interpolation for some and extrapolation from several thousand hours for the others in the case of 10^4 hours. Although no increase is

seen in the strength for 650°C and 10^3 hours up to the Ti/C value of about 0.4 with a tendency for even a slight decline, the strength increases rapidly as the Ti/C value rises further and shows the maximum value at around 1.2. Beyond this point, the strength demonstrates a tendency to decline with the increase in Ti/C. Similar tendencies are seen in the cases of 650°C and 10^4 hours and 700°C and 10^3 hours, but in the case of 700°C and 10^4 hours the strength is at its highest at the Ti/C ratio of about 0.8 with the peak position shifted toward the low Ti/C side.

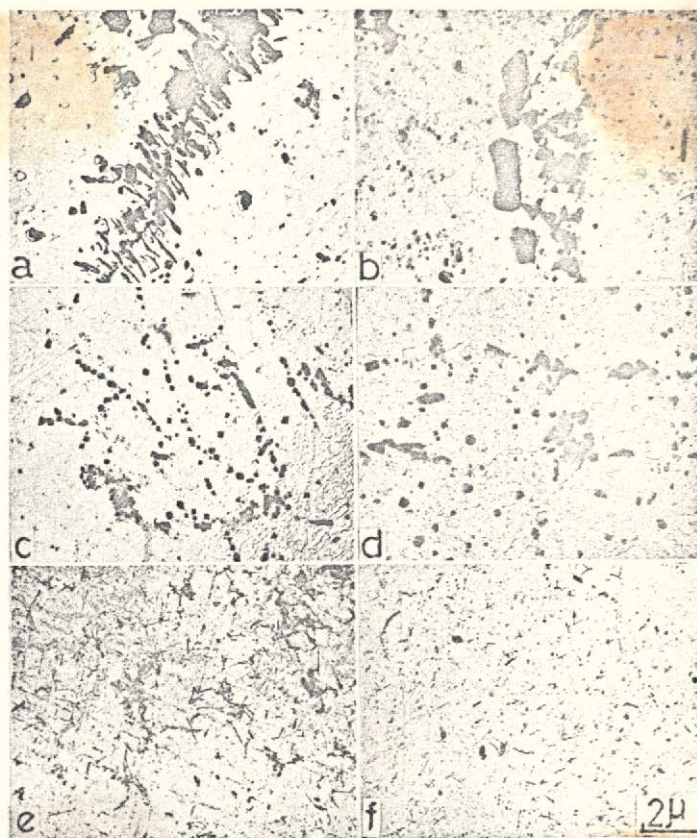
From these observations, it may be concluded that the high temperature strength is high in the Ti/C ratio interval of 0.8 - 1.2, with further additions of Ti leading to a decline in strength, and that on the high temperature, long time period side in particular, the maximum strength is obtained when the Ti/C value is slightly less than 1.

3.1.2 Structure

With respect to the structures of the various steels with Ti added, which were subjected to solid solution heat treatment at 1100°C for 1 hour, some minute undissolved carbides, apparently TiC, were detected in steels with more than 0.64% of Ti within the range of observation of the scanning electron microscope. But these carbides were hardly detectable in those with smaller amounts of Ti, so that it would seem that solid dissolving was almost complete in steels with low quantities of Ti.

Photo. 1 shows examples of electron micrographs of the structures of Ti1, Ti4 and Ti6 which were aged or creep-ruptured.

at 700°C. a) is the structure of Ti1 steel (Ti/C=0.13) aged for 1000 hours, and b) is the structure of the sample ruptured at 3620 hours. In both instances, somewhat coarse grain boundary carbides and $M_{23}C_6$ that has developed into triangular, flake-like forms are observed, and in the ruptured sample, a considerable amount of 781 precipitation is seen inside the grains as well. These structures are often seen in regular 18-8 steel, and in terms of strength also, Ti1 is equivalent to S1 without the added Ti. c) and d) are structures of Ti4 steel (Ti/C=0.77) in which flake-like $M_{23}C_6$ forms are observed after a short time period but no such $M_{23}C_6$ forms are seen at over 1000 hours. The strength for 700°C and 10^4 hours is highest at the Ti/C value of 0.77, and the agglomeration of carbides appears to be slow on the long time period side. In c) especially, $M_{23}C_6$ appears in granular forms in rows inside the gamma grains to show a precipitation morphology considerably different from that of a). As we shall discuss later, in the case of Nb, preferential precipitation of NbC on the dislocation is observed from time to time. In the case of Ti in the present experiment too, it is conceivable that TiC first precipitated on the dislocation and then, with this as the nucleus, the precipitation of $M_{23}C_6$ took place to form such bead-like precipitates. Since the Ti/C value of this steel is less than 1, the Ti obviously cannot fix all of the C so that the precipitation of $M_{23}C_6$ occurs in succession. But it is interesting that the precipitation of TiC occurs in the form of offering precipitation sites for this precipitation of $M_{23}C_6$. e) and f) are structural examples of Ti6 steel (Ti/C=2.0), a steel whose strength declines on the long time period side as indicated in Fig. 1.



a) Ti1 aged for 1000 hr b) Ti1 7kg/mm², ruptured at 3620 hr
 c) Ti4 aged for 1000 hr d) Ti4 10kg/mm², ruptured at 1179 hr
 e) Ti6 aged for 1000 hr f) Ti6 8kg/mm², ruptured at 2131 hr

Photo. 1. Electron micrographs of titanium added steels aged or creep-ruptured at 700°C (extraction replica).

After a short time period many granular TiC formations are observed inside the grains, but at over 1000 hours thread-like TiC formations appear everywhere inside the grains as seen in the photographs. These forms of TiC are also believed to have precipitated on the dislocations. They are also partially observed in Ti5, but are few quantitatively.

The rupture time ranges within which these thread-like precipitates are detected in the extraction replica observations are plotted against the Ti/C ratio of the samples to give the diagram in Fig. 3. Thread-like TiC formations are not detected in samples

with small amounts of Ti or short rupture time periods, and the precipitation range at 700°C spreads toward lower Ti/C ratio than that at 650°C. In other words, the tendency toward thread-like formations is greater in those samples with higher Ti/C values, longer rupture time periods and higher temperatures. On the other hand, since C could not be fixed sufficiently by Ti in the sample of Ti6 steel ruptured at 700°C and 2131 hours either so that the presence of $M_{23}C_6$, although quantitatively low, was detected, it can be assumed that $M_{23}C_6$ precipitates occur in all the samples.

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The results of electron beam diffraction of the thread-like precipitates seen in Photo. 1 (f) are shown in Photo. 2. a) is a bright field image from which it can be gathered that the minute precipitates constitute threads in complex, intertwining formations. On the basis of the diffraction image in b), these precipitates are identified as being mainly TiC , but diffraction spots which were apparently caused by other diffraction phases were also observed in part.

3.2 Effects of Nb

3.2.1 Solid Solution Structure

A scanning electron micrograph of the structure of a solid solution treated sample of Nb8 steel is shown in Photo. 3. What looms in the center is delta ferrite, and the white, shiny granular formations are undissolved NbC. Judging from its distribution pattern, this undissolved NbC is assumed to have formed during solidification and remained without dissolving. Since this undissolved NbC was observed in relatively small amounts in Nb1, Nb3

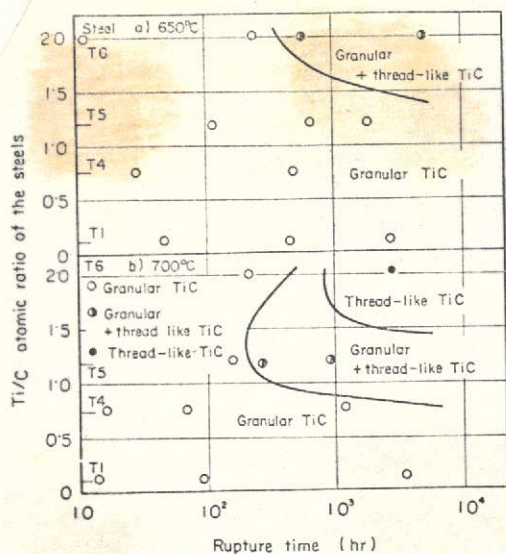
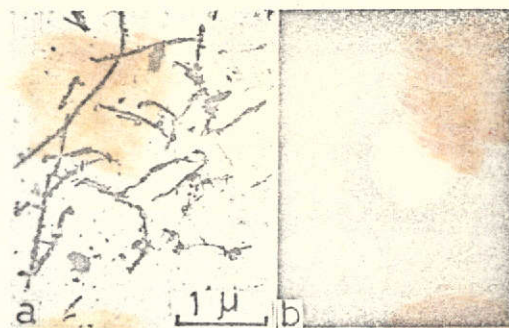


Fig. 3. Morphological diagram of precipitated carbide TiC in 18Cr-10Ni austenitic steels creep-ruptured at 650°C and 700°C.



Photo. 3. Delta ferrite and undissolved niobium carbide observed in Nb8 steel solution treated at 1200°C for 1 hr.



a) and b) Thread-like TiC and its diffraction pattern, respectively.
Photo. 2. Precipitated thread-like carbide TiC in Ti6 steel aged at 700°C for 1000 hr.

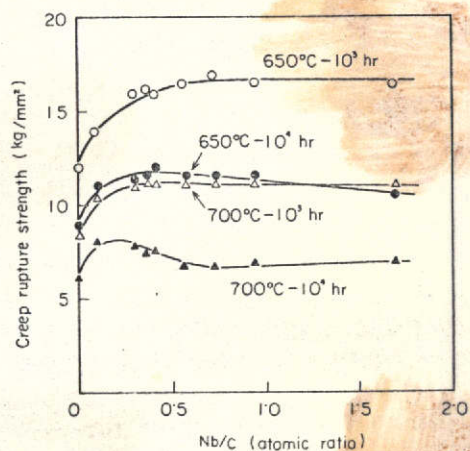


Fig. 4. Relationship between 10^3 hr rupture strength and Nb/C atomic ratio of the 16Cr-10Ni steels containing various amount of niobium.

and Nb5 steels, and in large amounts in Nb7 and Nb8, it may be assumed that Nb of up to the ratio of about $Nb/C=0.6$ can be dissolved to a considerable extent by means of solid solution treatment of 1200°C and 1 hour.

The amounts of delta ferrite were measured by means of line analysis. The results showed that there was practically none in Nb1, Nb3 and Nb5 steels, while there was 1.1% in Nb7 steel and



a) Nb1 aged for 1000 hr b) Nb1 8kg/mm², ruptured at 11930 hr
 c) Nb3 aged for 1000 hr d) Nb3 8kg/mm², ruptured at 7270 hr
 e) Nb7 aged for 1000 hr f) Nb7 14kg/mm², ruptured at 300 hr
 g) Nb8 aged for 1000 hr h) Nb8 9kg/mm², ruptured at 2980 hr

Photo. 4. Electron micrographs of niobium added steels aged or creep-ruptured at 700°C₂ (extraction replica).

3.6% in Nb8 steel. These results led us to surmise that part of the added Nb was perhaps concentrated in the delta ferrite. We therefore scanned the delta ferrite for Nb with the XMA, but in contrast to the inside of gamma, practically no increase in the Nb concentration could be observed in the delta ferrite. In fact, a tendency was observed for the concentration to decrease, so that

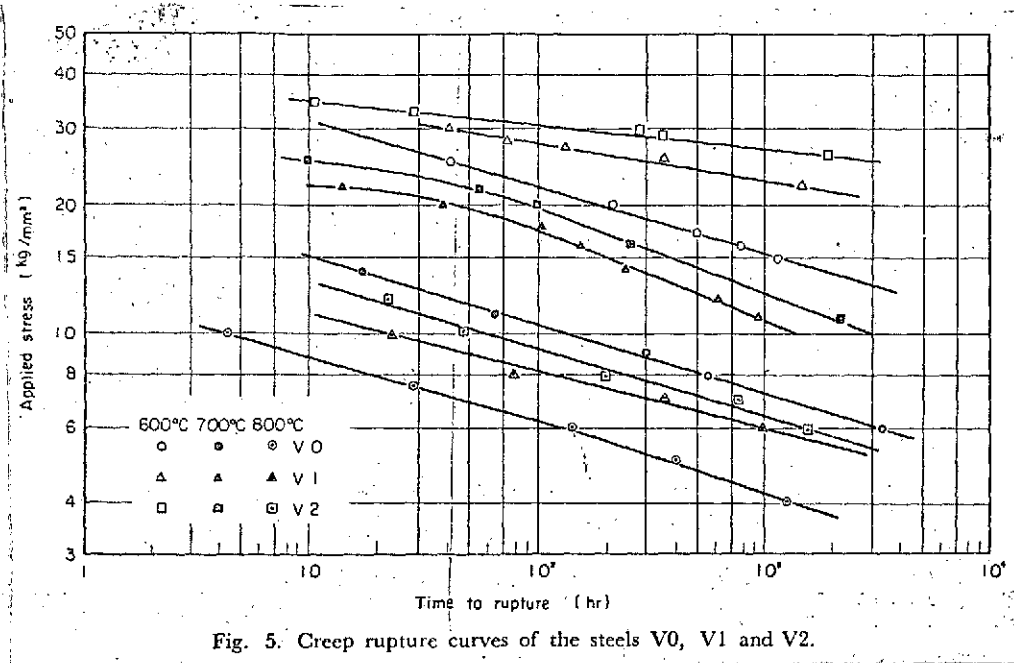


Fig. 5. Creep rupture curves of the steels V0, V1 and V2.

it may be assumed tentatively that Nb is distributed uniformly in the base.

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3.2.2 Creep Rupture Strength

The creep rupture strengths for 10^3 hours and 10^4 hours and 650°C and 700°C in the case of Nb1 - Nb8 steels with varying amounts of added Nb are shown organized according to the Nb/C (atomic ratio) of the samples in Fig. 4. With 650°C and 10^3 hours, the strength increases up to the Nb/C ratio of about 0.7, but beyond that, the strength does not vary very much with the increase in the Nb/C value. A more or less similar tendency is observed for the strength curves of 650°C and 10^4 hours and 700°C and 10^3 hours. They reach the maximum at the Nb/C value of about 0.4, but beyond there, increase in the Nb/C ratio is not accompanied by an increase in the strength. In fact, a tendency for even a slight decline is observed. This tendency is even more conspicuous for 700°C and 10^4 hours, in which

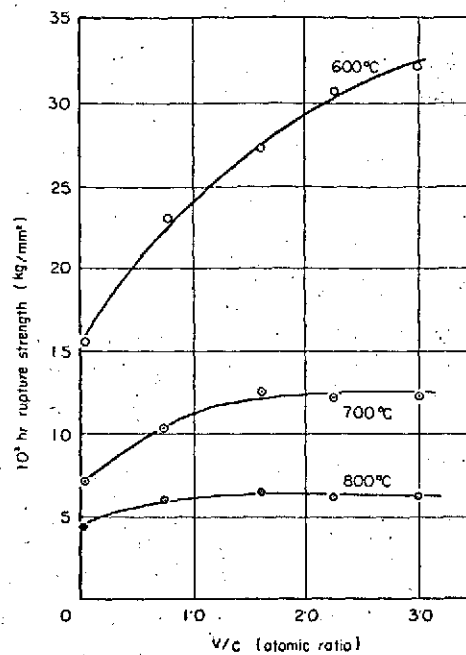


Fig. 6. Relationship between 10^3 hr rupture strength and V/C atomic ratio of the 16Cr-12Ni steels containing various amount of vanadium.

the maximum strength is demonstrated at the Nb/C value of about 0.2, with the strength declining as the Nb/C value increases further.

From the above findings, it may be assumed that in the case of 347 steel, which is currently in use with Nb/C ≥ 1 as the standard, it would be a better idea to decrease the amount of Nb when this steel is being used for purposes in which high temperature strength is important.

3.2.3 Structure

The representative structures of the aged and creep-ruptured samples of Nb1, Nb3, Nb7 and Nb8 steels at 700°C are shown in Photo. 4. a) is the aged structure of Nb1 steel (Nb/C=0.10) which has the highest rupture strength at 700°C and 10^4 hours, and rectangular

$M_{23}C_6$ precipitates are observed scattered inside the gamma grains. With the sample ruptured at 11930 hours in b), $M_{23}C_6$ precipitates of various shapes are distributed all over the inside of the grains and their agglomeration is quite slow. In the case of Nb3 steel (Nb/C=0.38) shown in c), the precipitation of $M_{23}C_6$ has occurred with the thread-like NbC, which has precipitated on the dislocations, as the nuclei. This phenomenon was also observed in the Ti steels. In d), the sample of the same steel ruptured at 7270 hours, granular NbC carbide formations become conspicuous. In Nb7 and Nb8 steels with greater Nb/C ratios, undissolved carbides are seen and the amount of $M_{23}C_6$ precipitates decreases. But what is interesting in comparing e) and g) with f) and h) is that while most of the NbC precipitates observed in the creep-ruptured samples are granular, the precipitation of NbC in the aged samples occurs mainly in thread-like formations. It is believed that this is due to some kind of effect creep deformation has caused in the nucleation and growth of the precipitates, but the particulars are not clear.

As demonstrated by the above findings, the creep-ruptured structures vary somewhat according to the value of Nb/C. In other words, whereas the precipitation of $M_{23}C_6$ occurs preferentially in the steels with low Nb/C ratios, delta ferrite or undissolved NbC formations are present in Nb7 and Nb8 steels and also, the precipitation phase is mostly NbC with a little $M_{23}C_6$.

3.3 Effects of V

3.3.1 Creep Rupture Strength

The creep rupture curves of V0 - V4 at 600°C, 700°C and 800°C are shown in Fig. 5. In the case of 600°C, the rupture strength at 10^3 hours is observed to be higher than V0 with no V added by about 8 kg/mm² for V1 and by about 11 kg/mm² for V2. In addition, the creep rupture curve gradients of both V1 and V2 are considerably milder than that of V0, and the improvement in strength by the addition of V becomes more marked as the curves approach the long time period side. In the case of 700°C too, the strengths of V1 and V2 are higher than that of V0, but the tendency of the stress-rupture curves is slightly different from the case of 600°C. In other words, the gradients of V1 and V2 on the short time period side do not vary much from the gradients at 600°C, but on the long time period side they become more or less parallel to the V0 curve. At 800°C V1 and V2 again demonstrate greater rupture strengths than V0, but a bending of the curves, such as the one observed at 700°C, is not seen this time. Similar tendencies are observed for V3 and V4 but there is practically no difference in the strengths of these two steels which demonstrated about the same strengths as that of V2 except in the case of 600°C.

The conspicuous changes in the gradients of the creep rupture curves caused by the test temperatures, as indicated above, are peculiar to steel with added V and are usually not seen in the case of other added elements. Even with the comparative sample of V0 steel, the creep rupture curves of the various temperatures are more or less parallel.



Photo. 5. Electron micrographs of vanadium added steels creep-ruptured at 700°C (extraction replica).

Fig. 6 shows the relationships between the V/C atomic ratios of the samples and the 10^3 hour rupture strengths at the different temperatures. At 600°C, the increase in V/C ratio is accompanied by an increase in the 10^3 hour rupture strength. With 700°C too, the strength rises with the increase in V/C ratio, but the strength approaches a constant value in the vicinity of V/C=1, and it is shown that any further increase in V does not contribute much to the improvement of strength. An increase in strength due to the addition of V is again observed in the case of 800°C, but its effect

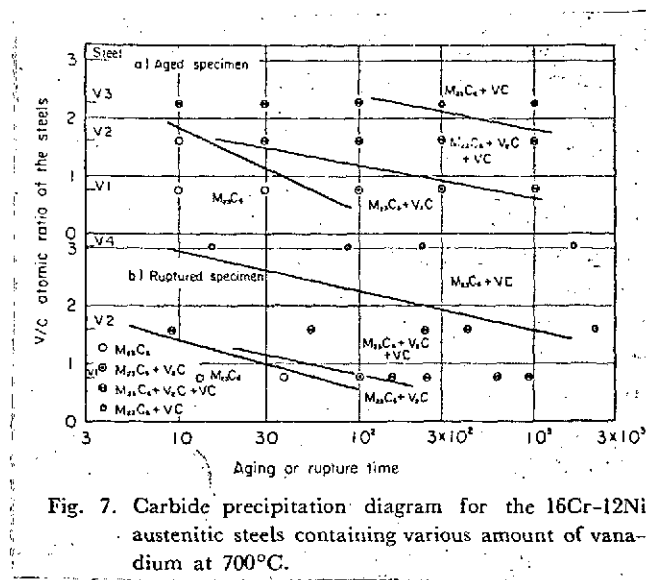


Fig. 7. Carbide precipitation diagram for the 16Cr-12Ni austenitic steels containing various amount of vanadium at 700°C.

is much smaller compared to the cases of 600°C and 700°C.

3.3.2 Structure

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The observation of structure was conducted by means of extraction replicas from the samples creep-ruptured at 600°C, 700°C and 800°C. At 600°C, the coarsening of the grain boundary carbide $M_{23}C_6$ is slightly accelerated with increase in the amount of V added, but practically no coarsening tendency was observed in the $M_{23}C_6$ precipitating inside the grains. In addition, during the identification of the precipitation phase by means of selected area electron beam diffraction, practically no V carbides (nitrides) were observed and only $M_{23}C_6$ was detected.

Next, examples of the structures of samples creep-ruptured at 700°C are shown in Photo. 5. a) is the structure of the V1 steel sample ruptured at 110 hours. $M_{23}C_6$ which has grown along the gamma grain boundary and granular V_2C precipitates [19] beside it are seen. b) is the sample again of V1 steel, ruptured at 239 hours.

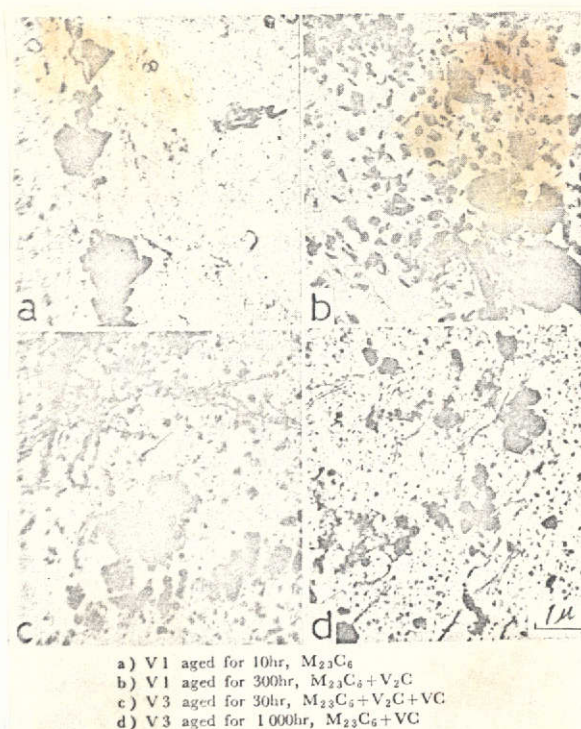


Photo. 6. Electron micrographs of vanadium added steels aged at 700°C (extraction replica).

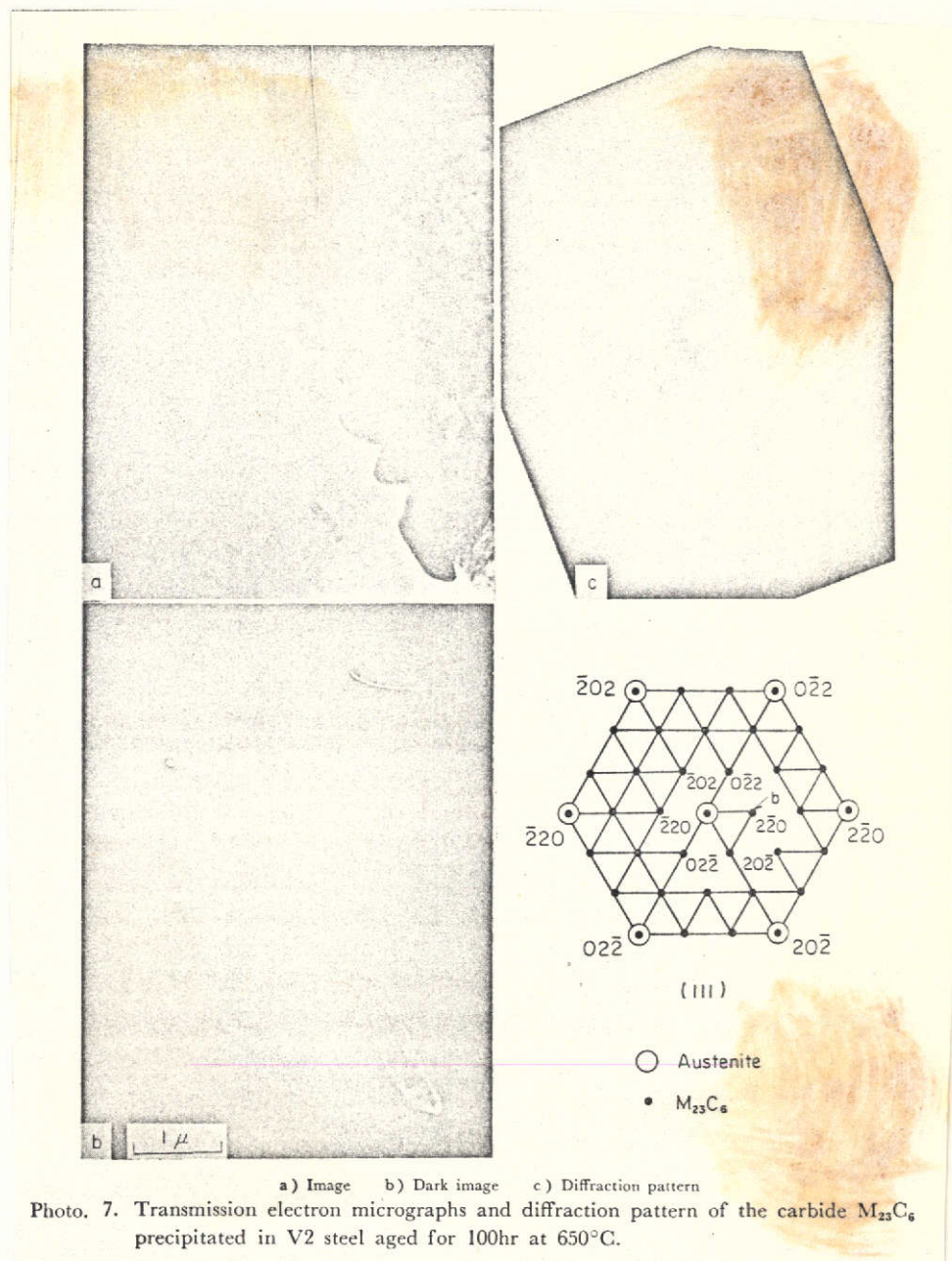
Here, $M_{23}C_6$ on the gamma grain boundary and granular V_2C inside the grain are observed. In c), the V1 steel sample ruptured at 946 hours, the rod-like and rectangular-shaped precipitates are $M_{23}C_6$ according to the result of identification, and between these are observed granular V_2C and thread-like precipitates. These thread-like precipitates are VC, to be discussed later, which was not detected in the cases of short rupture time periods. d) is the V2 steel sample ruptured at 55 hours, and here the precipitation of V_2C has occurred. In e) where the rupture time period is longer, $M_{23}C_6$ which has precipitated in a plate-like shape on the grain boundary is observed together with thread-like VC which has precipitated beside it. Inside the grain, granular V_2C can be observed in some parts as shown by f). In the case of V4 steel with a large amount of added V, the $M_{23}C_6$ carbide which has precipitated on the

grain boundary and thread-like VC are seen in the structure g) of the sample ruptured at 15 hours, but granular V_2C can be hardly detected. In the sample h) ruptured at 229 hours, too, there are only the $M_{23}C_6$ precipitated along the grain boundary and thread-like VC, but here, the amount of precipitation of thread-like VC is larger. In i) with a longer rupture time period, the coarsening of $M_{23}C_6$ on the grain boundary is conspicuous.

From these findings in the observation of the creep-ruptured samples at $700^{\circ}C$, it was verified that the precipitation of $M_{23}C_6$ in all ruptured samples containing V occurs mainly on the grain boundaries. Granular V_2C was found in V1 and V2 steels ruptured in less than about 500 hours, while thread-like VC was detected in V1 steel ruptured at about 1000 hours, in V2 steel samples ruptured at more than about 500 hours, and in all ruptured samples of V4 steel.

In the structural observation of creep-ruptured samples at $800^{\circ}C$, 2 types of precipitates, namely $M_{23}C_6$ carbide and thread-like VC, were found, but granular V_2C was not detected. A tendency was observed for the amount of precipitation of thread-like VC to increase with greater amounts of added V and with longer rupture time periods.

Next, some representative structures of samples aged at $700^{\circ}C$ are shown in Photo. 6. Compared to the creep-ruptured samples, there are no conspicuous differences seen in the structures of the aged samples. In a), the V1 steel sample aged for 10 hours, lumps of $M_{23}C_6$ which have precipitated on the grain boundary are seen. When the aging period reaches 300 hours in b), small, granular V_2C



precipitates occur beside the $M_{23}C_6$. c) is V3 steel which contains a large amount of V, and in this case, granular V_2C and thread-like VC are already present together after an aging period of 30 hours. In d) with the much longer aging period of 1000 hours, the structure consists entirely of $M_{23}C_6$ and thread-like VC with granular V_2C no longer detected.

As the findings above show, the types of precipitating carbides vary according to the amount of V and the heating period. These relationships at 700°C can be expressed as shown in Fig. 7. In other words, in aged specimen a) $M_{23}C_6$ is found in all the samples, and the amount of precipitation therein increases with longer aging periods. Granular V_2C is precipitated only in steels with certain specific amounts of V, and furthermore, the precipitation occurs before that of thread-like VC at a certain stage of advancement of the aging process. In addition, the thread-like VC increases with greater amounts of V and longer aging periods. No conspicuous differences are observed in ruptured specimen b) when compared to the aged specimen, with the precipitation of the same types of carbides being detected for the same retention times at 700°C. It would seem that in the case of creep-ruptured samples, unlike in the case of aged samples, the stress load would affect the precipitation process. In the case of steels with added V, however, all it does is to advance the precipitation period of the carbides slightly, so that its effects are not seen conspicuously in the forms or the distribution of the precipitated carbides. In a similar structural diagram prepared for 650°C, the types of precipitating carbides were the same as for 700°C, but the advancement of their precipitation was slower. It was observed that when V3 steel of $V/C=2.26$ was aged for 1000 hours at 650°C, V_2C still did not disappear.

3.3.3 Electron Microscope Observation and Identification of Precipitates by Means of Thin Film

Transmission observation by means of the electron microscope

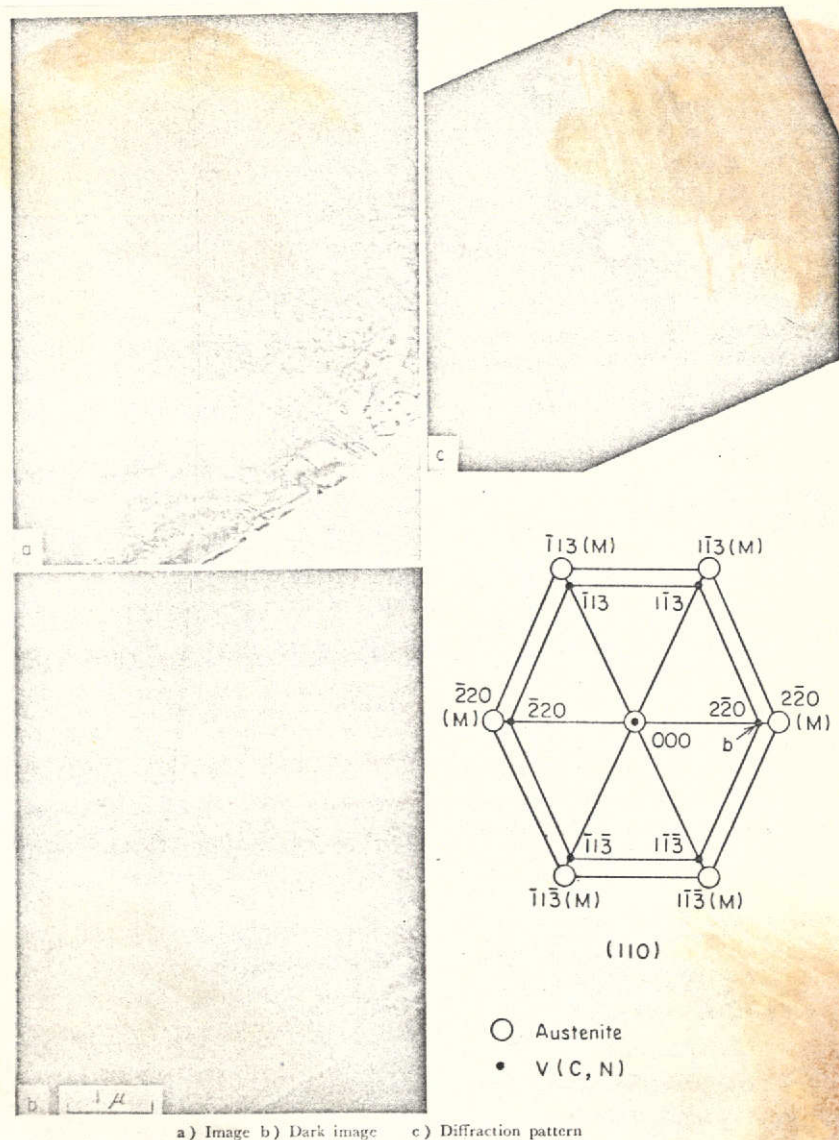


Photo. 8. Transmission electron micrographs and diffraction pattern of thread-like carbide VC precipitated in V2 steel aged for 100hr at 650°C.

and identification by means of electron beam diffraction were conducted on representative carbides which were observed in Photo. 5 and Photo. 6. Photo 7 a), a bright field image, shows carbides which have precipitated on the grain boundary. Such precipitates were detected in large numbers in the extraction replicas as well. The dark field image b) was obtained from the diffraction spot which appears at a point $1/3$ of the way across the base in the

electron beam diffraction image c) (point b in the key diagram).

The dark field image indicates that the above-mentioned diffraction spot is due to a grain boundary precipitate. Like the base, this precipitate is a cubic system with the precipitation occurring under the same orientational relationship. Assuming that the lattice constant of the base is 3.534 \AA as obtained through X-ray diffraction, the lattice constant of this precipitate is calculated to be 10.60 \AA . The lattice constant of Cr_{23}C_6 is reported to be 10.638 \AA [20] while the above-mentioned value of 10.60 \AA is slightly less, so that the precipitate can be considered to be M_{23}C_6 in which part of the Cr in Cr_{23}C_6 has been substituted by other elements (Fe, V, etc.).

Photo. 8 a) is a precipitate inside the grain, and judging from its precipitation morphology, it would seem to be the same as the thread-like precipitates shown in the extraction replica of Photo. 6 d). In the dark field image b), which was photographed using a small spot inside the base spot, the thread-like precipitate is luminous. But since some parts are more luminous than others, a further study is necessary in order to clarify the detailed form and structure of this precipitate. From the diffraction pattern c), it is seen that the precipitate is a cubic system like the base and that its precipitation occurs under the same orientational relationship. This coincides with the finding by Silcock [18] that carbide V_4C_3 has a cube-cube orientational relationship with its base. Also, the lattice constant of this thread-like precipitate is calculated from the lattice constant value of the base to be 4.06 \AA . By comparing it to such data as VC (14%C, 4.16 \AA , cubic) [20]

and VN (0.72N, 4.066 Å, cubic) [21] in the bibliography, and by taking the chemical composition of the sample into account, the precipitate could be considered to be V carbide (nitride), V(C, N), in which part of the carbon in VC has been substituted by nitrogen.

4. Discussion

As stated earlier, the optimal addition amounts of Ti and Nb for the improvement of the high temperature strength in 18-10 Ti steel and 18-10 Nb steel vary according to the temperature used and the desired life-time. In the case of Nb steel, for example, Nb/C values of over 0.7 are suitable for rupture strength at 650°C and 10³ hours, while values of around 0.2 - 0.3 give the maximum strength for rupture strength at 700°C and 10⁴ hours. In the case of Ti steel, too, the Ti/C value is optimal at about 1.2 for rupture strength at 650°C and 10³ hours, while Ti/C of 0.8 demonstrates the maximum rupture strength at 700°C and 10⁴ hours. Since the optimal addition amounts vary according to the conditions of use in this manner, it is not possible to define fixed addition amounts. But at any rate, the conventional concept in corrosion resisting steel that C is fixed adequately by making the Ti/C or Nb/C atomic ratio more than 1 is not just unsuitable for heat resisting steel. The addition of excessive amounts of Ti or Nb tends to destroy the effects of the addition of the suitable amounts, with this tendency becoming more pronounced on the high temperature, long time period side. In other words, the compositions of the conventional 321 and 347 steels can hardly be termed optimal when seen from the viewpoint of high temperature creep rupture

strength alone. It is believed, therefore, that when Ti or Nb is being added to steel for the purpose of heat resistance, suitable addition amounts must be selected on the basis of the conditions of use.

It also became apparent from the results of this experiment that V, which is rarely added to heat resisting steel, can improve creep rupture strength considerably. It is believed that V can become an effective alloying element with respect to high temperature strength if deterioration of resistance to high temperature oxidation could be prevented. In particular, creep rupture strength at 600°C is improved markedly by the addition of V, and this effect becomes stronger toward the long time period side.

In the past, it has been thought that the high temperature strengthening mechanism of Ti or Nb in 321 or 347 steel involved the precipitation of Ti or Nb in the form of stable MC type carbides which increased the creep resistance. But in actuality, it may not necessarily be that simple. First of all, the morphology of the precipitation of the MC type carbides, particularly form, size and distribution, must vary according to the addition amount, temperature, stress and so on, so that its contribution to strength would naturally change also. Furthermore, these MC type carbides undergo changes other than precipitation and agglomeration. As observed in Ti steel, some change their morphology, or, as in the case of V steel, some change from V_2C to VC. In addition, even in steels in which C is considered to be adequately stabilized by Ti, Nb and V, the incidental precipitation of $M_{23}C_6$ takes place, while even more precipitation of $M_{23}C_6$ occurs in steels with small

amounts of Ti, Nb and V.

These phenomena make it even more difficult to establish a sufficient correlation between creep strength and structural changes, but within the scope of this experiment, the following 4 points may be cited as the principal factors in the high temperature strengthening effect of strong carbide forming elements such as Ti, Nb and V.

1) Carbides precipitated in granular form in a gamma base contribute to improvement in creep resistance. This is supported by the fact that granular MC type carbides are often observed in Ti steel or Nb steel and by experimental results showing corresponding increases in creep strength. A remarkable increase in creep rupture strength at 600°C with the addition of V is believed to be due to the solid solution strengthening effect of V together with the inhibition of the agglomeration of $M_{23}C_6$ precipitating inside the grains, which maintains the strengthening effect of its dispersion inside the grains over a long period of time. Within the range in which the precipitation of granular V_2C is observed in a sample ruptured at 700°C, the creep rupture curve does not yet show a bend but shows high rupture strength. From this, it is believed that granular precipitation inside the gamma grains contributes to the improvement of high temperature strength.

2) With the periphery of the MC type carbides as its precipitation site, $M_{23}C_6$ is precipitated with good dispersion not only on the grain boundaries but also on the inside of the gamma grains. As seen in the aged samples of Photos 1 and 4, $M_{23}C_6$ is observed growing with the MC carbides as its nuclei. There is thus a cor-

relation between the precipitation of $M_{23}C_6$ and the precipitation of MC, and it is believed that the dispersed precipitation of $M_{23}C_6$ inside the gamma grains is accelerated by the presence of MC.

3) MC type carbides precipitated on dislocations obstruct the dislocation movement. It is often observed that NbC carbide is easily precipitated on defects such as dislocations during aging at high temperatures. It is to be expected that such a type of precipitation would occur during creep deformation as well, and it is easily supposed that there would be some kind of interaction between this type of precipitation and dislocation. Also, a large amount of thread-like V carbides was found in steels with V added, and it is believed that these also contribute to the strengthening effect by undergoing some sort of interaction with the dislocations.

4) In the increase of creep rupture strength in steels with added V at 600°C, the solid solution strengthening effect of V is believed to be playing a major role since the amount of precipitating V carbides is small and since most of the V can be assumed to be dissolved in the gamma base. Ti and Nb are also believed to contribute to the strengthening effect by dissolving in the gamma base during stages at which their precipitation has not progressed sufficiently. The conspicuous increase in strengths demonstrated by the steels with added Ti on the short time period side in Fig. 1 is probably due to dissolved Ti.

These actions of the carbides and the dissolved elements mentioned above are believed to be the principal factors behind the increased strengths of the Ti steels, Nb steels and V steels, but in the case of the Ti steels, the strength declines on the

long time period side when the amount of Ti increases as shown in Fig. 1. The temperature and time range within which this strength decline occurs is similar to the range in which the precipitation of the thread-like TiC referred to in a section on structural observation occurs. The strength deterioration of high Ti steel on the long time period side has already been recognized by Gyōshun [8] and its correlation with needle-like precipitates of Cr_3C_2 has been suggested as the cause, but Cr_3C_2 was not detected within the scope of this experiment. In the case of V steels too, a tendency toward strength deterioration was observed on the long time period side of the creep rupture curves at 700°C which showed bends. Thread-like V carbides were also detected in this case. At 800°C , thread-like carbides were observed in all of the samples, and here again, the rupture strengths showed a tendency toward deterioration similar to that which was seen on the long time period side at 700°C . From these findings, it is supposed that the strengthening effect of carbide dispersion in the thread-like precipitates is weaker compared to that of the granular precipitates inside the gamma grains, and that a decline in rupture strength may be caused by the change in the form of the precipitates from granular to thread-like. As for the causes behind the smaller contribution of the thread-like precipitates to creep rupture strength compared to the granular precipitates, the following points are conceivable. The thread-like precipitates are in a state in which the carbides have undergone the so-called segregation process, so that the probability of their obstructing the dislocation movement is lower than in the case of the granular

precipitates in which the sizes of the individual carbides are smaller but the dispersion of the granular forms is uniform. Also, the thread-like precipitates can easily become the starting points of micro cracks during rupture. But these points are still within the realm of supposition, so that the particulars remain to be explored in future research.

It is also believed that in the discussion of the correlation between creep rupture strength and microstructure, the strength of the grain boundary and the strength inside the grain must be considered separately. It would seem that since the added elements Ti, Nb and V were either dissolved in the base or precipitated mainly inside the grains with practically no tendency for their segregation on the grain boundaries observed, they would have practically no effect on the strength of the grain boundary.

However, in the case of regular high Cr-Ni stainless steel which contains no Ti, Nb or V, preferential as well as coarse precipitation of $M_{23}C_6$ occurs on the grain boundaries, and it is maintained that such $M_{23}C_6$, rather than contributing to the strengthening of the grain boundaries, can easily become the origin of micro cracks [22]. On the other hand, when Ti, Nb and V are added, the precipitation of $M_{23}C_6$ occurs dispersed inside the grains and a tendency is observed for the $M_{23}C_6$ on the grain boundaries to decrease. From these findings, it is believed that Ti, Nb and V prevent the decline in grain boundary strength indirectly, but there is still need for investigation with respect to the particulars.

5. Conclusion

The effects of strong carbide forming elements Ti, Nb and V on the creep rupture strength and the structure of precipitated carbides in 18%Cr-10%Ni-0.1%C series stainless steel were studied and the following conclusions were obtained.

1) In the case of the addition of Ti, the rupture strength at 650°C and 10^3 hours reaches the maximum for the Ti/C (atomic ratio) value of 1.2, with the rupture strength declining with further increase in the Ti/C value. As the temperature becomes higher and the time period longer, this Ti/C ratio for maximum strength shifts toward lower values, so that in the case of 700°C and 10^4 hours the strength reaches the maximum at about 0.8.

2) In the case of steel with added Nb, saturation occurs at the Nb/C value of about 0.7 for the rupture strength at 650°C and 10^3 hours, but in the case of higher temperatures and longer time periods a further increase in Nb/C causes the strength to decline somewhat. In the case of the rupture strength at 700°C and 10^4 hours, the maximum strength is demonstrated at Nb/C of 0.2 - 0.4.

3) The creep rupture strength is also improved by the addition of V, but the effect of V is stronger on the low temperature side. The rupture strength for 10^3 hours improves with increase in the V/C atomic ratio at 600°C, but for 700°C and 800°C it reaches the maximum at the V/C ratio of about 1. Improvement in strength is not observed when the V/C ratio is increased further.

4) The increase in creep rupture strength caused by the addition of Ti, Nb and V is believed to be due largely to the fine, uniform dispersion of granular $M_{23}C_6$ precipitated inside the gamma

grains. It is supposed that the MC type carbides of Ti and Nb have the effect of accelerating the dispersed precipitation of these $M_{23}C_6$ carbides inside the gamma grains. Also, the marked increase in the creep rupture strength at 600°C caused by V is believed to be due in large part to the solid solution strengthening effect of V.

REFERENCES

1. Shinoda, Tanaka, Ishii, Mimino and Kinoshita: Tetsu to hagane [Journal of the Iron and Steel Institute of Japan], 56 (1970), 9, p. 1231.
2. W. Koch, A. Schrader, A. Krisch and H. Rohde: Stahl u. Eisen, 78 (1958), 18, p. 1251.
3. Kawabe and Nakagawa: Tetsu to hagane [Journal of the Iron and Steel Institute of Japan], 53 (1967), 1, p. 46.
4. Shinoda, Mimino, Kinoshita and Minegishi: Tetsu to hagane [Journal of the Iron and Steel Institute of Japan], 54 (1968), 14, p. 1472.
5. Miyoshi: Nihon kinzoku gakkai shi [Journal of the Japan Institute of Metals], 28 (1964), p. 604.
6. Miyoshi and Gyōshun: Tetsu to hagane [Journal of the Iron and Steel Institute of Japan], 53 (1967), 4, p. 570.
7. Miyoshi and Gyōshun: Sumitomo kinzoku [Sumitomo Metals], 19 (1967), 4, p. 67.
8. Gyōshun: Tetsu to hagane [Journal of the Iron and Steel Institute of Japan], 54 (1968), 5, p. 584.
9. Mimino, Kinoshita and Ihara: Nihon Kōkan gihō [Nippon Kōkan Technical Report], 44 (1968), p. 163.
10. Shinoda, Mimino, Kinoshita and Minegishi: Tetsu to hagane [Journal of the Iron and Steel Institute of Japan], 55 (1969), 2, p. 174.
11. Fujita, Araki, Yamada and Nakamura: Tetsu to hagane [Journal of the Iron and Steel Institute of Japan], 57 (1971), 4, p. 211.

12. Mori, Inoue, Ōoka and Takemura: Tetsu to hagane [Journal of the Iron and Steel Institute of Japan], 57 (1971), 11, p. 533.
13. Yamada and Fujita: Gakushin 123-1 kenkyū hōkoku [Report of Committee No. 123, Japanese Association for the Advancement of Science], 12 (1971), 2, p. 105.
14. Yamada and Fujita: Gakushin 123-i kenkyū hōkoku [Report of Committee No. 123, Japanese Association for the Advancement of Science], 12 (1971), 3, p. 243.
15. Nakagawa, Kawabe and Otokuro: Kinzoku Zairyō Kenkyūsho kenkyū hōkoku [Report of National Research Institute for Metals], 8 (1965), 6, p. 431.
16. Nakagawa and Otokuro: Kinzoku Zairyō Kenkyūsho kenkyū hōkoku [Report of the National Research Institute for Metals], 4 (1961), 3, p. 210.
17. J. J. Irani and R. T. Weiner: JISI, 203 (1965), p. 913.
18. J. M. Silcock: Acta Metal., 14 (1966), p. 687.
19. Tanaka, Shinoda and Ishii: Tetsu to hagane [Journal of the Iron and Steel Institute of Japan], 56 (1970), 10, p. 1406
20. ASTM card (1961)
21. W. B. Pearson: Handbook of Lattice Spacings and Structures of Metals, Pergamon Press (1967), p. 439, p. 455.
22. Imai and Masumoto: Nihon kinzoku gakkai kaihō [Bulletin of the Japan Institute of Metals], 1 (1962), 6, p. 411.